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THE RECYCLING OF FLUORIDE IN COAL REFINING

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(57) Claim

1. A process for recycling fluoride following demineralizing bituminous coal or other mineral containing carbonaceous material by leaching the carbonaceous material with an aqueous fluoride etchant solution, the improvement comprising reacting the spent leachant with a water soluble hydroxide ion source to precipitate at least some of the minerals dissolved in the leachant, removing the precipitate therefrom and treating the resultant fluoride solution to regenerate an effective fluoride etchant solution.

COMMONWEALTH OF AUSTRALIA

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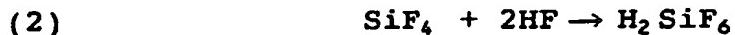
Complete Specification for the invention entitled:

The Recycling of Fluoride in Coal Refining

The following statement is a full description of this invention
including the best method of performing it known to us:-

BACKGROUND TO THE INVENTION
CHEMICAL DEMINERALISATION WITH DILUTE SOLUTIONS OF
HYDROFLUORIC ACID

It has been shown by earlier investigators that aqueous
5 solutions of hydrofluoric acid can reduce the ash content of
brown and bituminous coal dramatically. Whereas "ordinary"
mineral acids such as sulphuric, hydrochloric, phosphoric or
nitric acid show only attack on carbonates, and to some
extent on phosphates and oxides, they leave other mineral
10 matter like silicates and silicoaluminates with coal
undissolved. In contrast, dilute solutions of hydrofluoric
acid or its ammonium salt (ammonium bifluoride) dissolve
complex silicates and aluminates with ease at ambient
temperature. However, the direct treatment of coal as mined
15 gives quite often disappointing results when contacted with
HF. The reason for this is the formation of insoluble
silicofluorides of mainly Ca, K and Na which are sparingly
soluble and cannot be removed from the coal by washing:



Thus, calcite on the coal will react with
hydrofluoric acid to give not only calcium fluoride
(insoluble), but also calcium silicofluoride. The same
holds true with sodium and potassium or magnesium.

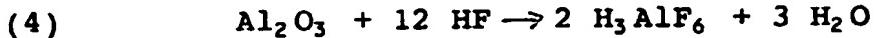
30 Ammonium silicofluoride, however, is soluble.

It is therefore a necessary pre-requisite for the
successful application of reactions (1) and (2) to remove
cations from coal prior to fluoride treatment. Then, in
the presence of excess hydrofluoric acid, the initially
35 formed silicon tetrafluoride, a gaseous substance at room

temperature, dissolves to form silicofluoric acid, H_2SiF_6 , which is the compound known by its trivial name "fluoride" when added to the major water supplies in a number of Australian cities. H_2SiF_6 being

- 5 water-soluble, can thus be washed out from the coal. Similarly, aluminium oxide found on coal reacts with HF to give soluble complexes, such as H_3AlF_6 (see equation 4), which can also be washed out together with silica, thus leaving a highly demineralised coal:

10



In previous laboratory work, cations interfering with the successful demineralisation of coal were easily 15 solubilised by hot hydrochloric acid²⁹. It could now be shown that the pre-treatment of coal with cold sulphuric acid as outlined in Part 1 of this report is also quite effective for this purpose. If this pre-treatment is ignored, HF will not be efficient enough in demineralising 20 coal to the desired low levels. A recent publication³¹ has suggested using 10% aqueous NH_4HF_2 in conjunction with an organic acid and HCl for ash removal from coal. However, this might only apply if the silica-alumina content is a minor constituent of the mineral matter.

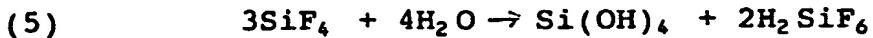
25 In order to meet more than the stoichiometric requirements of the reaction, an excess of HF has been used throughout this work, i.e., aqueous solutions of 20% HF (40% commercial grade diluted with water). This, however, does not mean that the acid could not be used in 30 more dilute form or as ammonium bifluoride. It would be left to the experimenter to determine the optimum concentration, especially with regard to possible safety hazards. Solid ammonium bifluoride could have some advantage in handling or storage over the aqueous (70%) 35 acid, commercially available. However, plastic materials

must be used instead of glass or earthen-ware since HF attacks these materials.

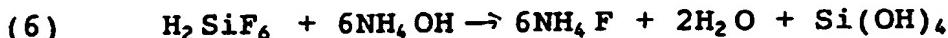
The reaction between the mineral matter and HF is slightly exothermic and dissolution of silica/alumina is fast. In small-scale laboratory work plastic beakers and a magnetic rod (Teflon coated) can be used for stirring. Filtration is best carried out on polycarbonate or polypropylene Buchner flasks and funnels, using hardened filter paper (Whatman No. 54). Other techniques which can be used are centrifugation of excess acid in plastic tubes, or, less sophisticated, washing by decantation. After complete acid removal for recovery, the coal can now be used for low ash coke manufacture or ground very finely for use in coal slurry combustion. Although the use of ultraclean coal as a substitute for fuel oil looks promising, it would take a good deal of persuasion for industry to initiate demineralising of coal by chemical methods. Low-ash coke manufacture could be a good start, followed by large scale, brown coal demineralisation by chemical methods, and finally by de-ashing bituminous coals. The export of large shipments of demineralised coal suspensions, which have been stabilised by additives in conventional oil tankers, should pose no major problem since the behaviour of coal suspensions in simulated shipping trials was well under study as witnessed by the author in Japan as far back as 1978.

THE RECYCLING OF FLUORIDE AND BYPRODUCTS OF THE PROCESS

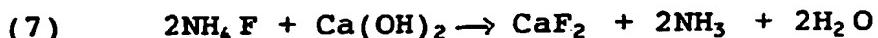
In the previous section it was mentioned that SiF_4 is a gas at room temperature, soluble in excess HF. On evaporation of the solution, or by passing through the solution a warm or hot carrier gas, SiF_4 can be removed from a partially closed reaction vessel. Subsequent hydrolysis gives pure silica as a gel and more silicofluoric acid in pure form:



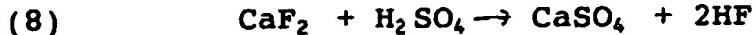
This reaction, however, does not recycle any fluoride and it would be necessary to modify the chemical pathway
5 accordingly to achieve this. One of the numerous possibilities is to neutralize the silicofluoric acid with ammonia, and add an excess in order to precipitate silica:



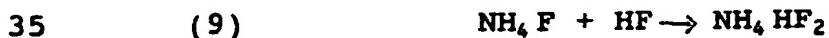
10 The ammonium fluoride is filtered from the silica and can be re-used for HF recovery in two ways:
a) The ammonia acts as a recyclable intermediate and can be liberated by lime addition to give insoluble calcium
15 fluoride and ammonia gas. The latter is liberated from the solution by heating:

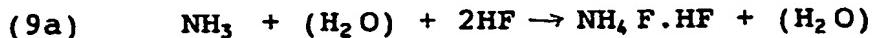


20 The calcium fluoride thus formed, which is free from silica, can be converted to hydrofluoric acid, using known techniques:



25 b) The ammonia acts as a vehicle for HF, i.e., ammonium bifluoride has in solution the demineralising power similar to HF according to equations (1) and (2). The intermediate silicofluoride complex formed is converted
30 back to fluoride by addition of excess ammonia (see equation (6)) and silica can be removed by filtration. The excess ammonia can be recovered by distillation or used for in situ generation of bifluoride according to:





This would mean that ammonium bifluoride is continuously generated by addition of hydrofluoric acid and ammonia.

- 5 However, ammonia fluoride is fortunately not very stable and disintegrates on heating of a solution to give ammonia and ammonium bifluoride according to



10

- This would allow the ammonia to be recovered by distillation, and the ammonium bifluoride solution would then just undergo a concentrating treatment to the stage where it would regain its dissolving power for the
15 minerals on coal.

Hydrofluoric acid distills at 111°C as a constant boiling azeotrope (43.2% HF). This would simplify its recovery from the filtrate, if waste heat was available, by first expelling SiF₄ (see above) and distillation of
20 the azeotrope. If no pure silica was required, the filtrate, containing HF and H₂SiF₆, from the coal treatment step, could be neutralized with ammonia, giving silica gel, contaminated with other compounds.

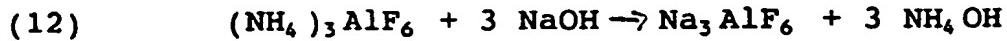
The chemistry of fluoride recycling with regard to
25 aluminium is not quite as straightforward, since aluminium fluoride reacts with ammonium ions to form the insoluble ammonium-analog to cryolite:



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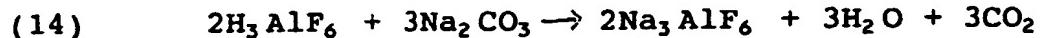
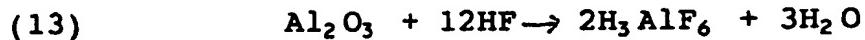
This precipitation of aluminium occurs already at low pH values (4-5), and would allow a selective preparation of coal-derived aluminium from silica, which would precipitate mainly in the alkaline region. It is possible
35 to convert the ammonium cryolite to the sodium compound,

by simple alkali treatment:



5 Cryolite is the electrolyte used for electrolysis of alumina. Cryolite can be regarded as the sodium salt of the hypothetical aluminofluoric acid. It is technically prepared by dissolving aluminium oxide in HF and treatment with soda:

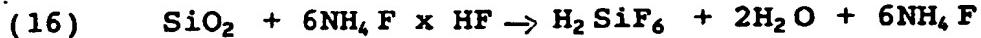
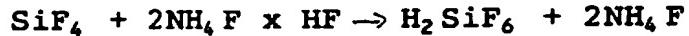
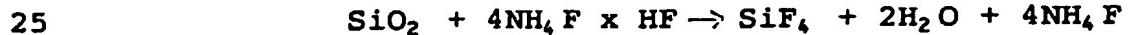
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15 If the recovery process was geared for pure silica (equation 5), silicon tetrafluoride would be removed from the coal leaving behind ideally aluminofluoric acid in solution, from which cryolite would form according to equation (14).

20 RECYCLING OF FLUORIDE USING THE AMMONIUM BIFLUORIDE ROUTE

The use of ammonium bifluoride as a vehicle for HF in coal demineralisation requires the modified stoichiometry of equation (1):



30

The silicofluoric acid formed as intermediate is destroyed by ammonia addition (equation 6) and the silica removed by filtration. Excess ammonia is recovered by distillation and the remaining ammonium fluoride can 35 either be converted by addition of hydrofluoric acid to

give ammonium bifluoride or by further evaporation of the filtrate, whence decomposition to ammonia bifluoride occurs (equations 9 and 10).

Thus, fluoride recycling is much simplified and 5 requires only a heating step after the removal of silica by filtration. The recovery of the demineralizing reagent and its regeneration using this route has the potential to substantially reduce the processing costs.

The present invention relates to an improvement in 10 methods for demineralizing carbonaceous materials and more particularly to improved methods in which fluoride etchant solutions are recovered, regenerated and recycled.

It is widely known that derivatives of fluorine such as hydrofluoric acid, HF, or its salts, in particular its 15 ammonium salts such as $\text{NH}_4\text{F} \cdot [\text{HF}]_x$, where $x = 1, 2, 3$ or 4, attack silicious material commonly practised in glass etching. This attack is not restricted to silica but can be observed on other oxides, such as alumina in particular, if the latter forms part of the molecular 20 structure in silicates. Aqueous solutions containing fluorine compounds which are effective in dissolving silica and/or alumina, and/or other mineral oxides are hereinafter called "aqueous fluoride etchant solutions". Such silicates are present in coals, and hence can be 25 removed partially or totally from coal by leaching with fluoride solutions under moderate conditions. Depending on the composition of ash forming constituents in coal a pre-treatment of this coal with acidic reagents such as mineral acids might or might not be necessary. A previous 30 patent (Australian Patent 472,900) describes the demineralization of brown coals down to low ash levels with aqueous solutions including the use of fluorides. The latter are used as a final step in order to remove residual mineral matter from coal which cannot be removed 35 by any other type of aqueous reagents.

Other processes for producing low ash coal involve dissolving mineral constituents in molten alkalis or in aqueous alkaline solutions at elevated temperatures and pressures and the removal of thereby formed alkali-stable
5 minerals by subsequent acid leaching of the coal. The low-ash coal thus obtained may, in some circumstances, contain more silica or alumina than is desirable, and it may therefore be expedient to give it a final treatment with fluoride solutions.

10 Major problems which have prevented the large scale production of ultraclean coal and its derivative such as coke by the fluoride route have arisen from either the cost or the chemical properties of hydrofluoric acid and fluorides. These problems which cover economic,
15 environmental and health aspects, would largely disappear if a simple, efficient and economic method were available to recover, regenerate and recycle the fluorine compounds.

Fluorine recovery schemes previously proposed, although not after coal refining, usually require high
20 temperature processing to release hydrogen fluoride gas, followed by its collection as an aqueous solution which may well be more concentrated and hence more corrosive than is actually required for re-use in the demineralizing process. This could cause operating problems and thus
25 preclude its use in coal refining.

A major object of the present invention is to provide a practical means of achieving good recovery and re-use of reagents under mild and easily manageable conditions after coal refining so that the fluoride route could be used
30 industrially to produce low-ash coal, and concurrently to recover the inorganic constituents either as useful byproducts or as innocuous wastes.

The fluoride route could also be employed in the final ash removal from black coals which have undergone an
35 alkali-acid purification step and for brown coal which had

undergone an ion-exchange treatment step with mineral or other inorganic or organic acids.

The present invention consists in a process for demineralizing bituminous coal or other mineral containing 5 carbonaceous material by leaching the carbonaceous material with an aqueous fluoride etchant solution, the improvement comprising reacting the spent leachant with a ~~water waste~~ soluble hydroxide ion source to precipitate at least some of the minerals dissolved in the leachant, removing 10 the precipitate therefrom and treating the resultant fluoride solution to regenerate an effective fluoride etchant solution.

The process to be described may be applied to the treatment of a wide range of coals, either in the as-mined 15 condition or after preliminary cleaning by other methods. The use of acidic heavy media as described in a co-pending Australian patent application No. PI1784 has been found very suitable for this purpose.

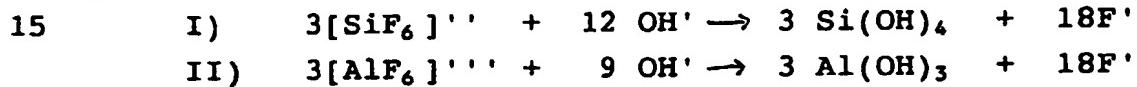
In its broadest form the present invention is 20 applicable to spent aqueous fluoride leachants derived from the demineralization of coal or other carbonaceous materials. These leachants contain silicon, aluminium and other elements in solution as complex compounds or otherwise. For instance silicon which is usually a major 25 inorganic component is present wholly or partially as fluorosilicic acid, H_2SiF_6 or its salts. Likewise, aluminium is present wholly or partially as fluoroaluminic acid H_3AlF_6 or its salts. The composition of the leachant should be optimized so that it gives the best 30 demineralizing effect and facilitates reagent recovery, regeneration and recycling. The invention includes the use of fluorides which can be seen as mixtures of ammonium fluorides, as stated earlier with hydrofluoric acid which demineralize coal on contact with the latter by forming 35 the aforementioned complexes. This contact is preferably



facilitated in vessels inert to fluoride and the time of contact may vary depending on the granular size of the coal. Dissolution of minerals is achieved accordingly within a matter of minutes on finely crushed coal or

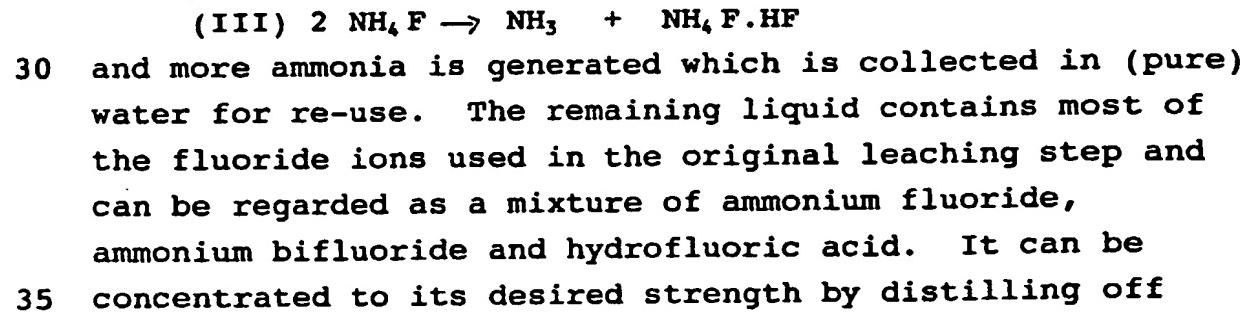
- 5 within a matter of hours on coarser material. The temperature of the solution may be kept ambient or can be elevated to just below boiling point of the solution.

- According to the invention the spent leachant, after separation from the leached and largely demineralized
10 coal, is treated with ammonia gas or ammonium hydroxide, preferably at or near ambient temperature to decompose the soluble inorganic compounds and thereby to precipitate silica, alumina, and other oxides present in hydrated or gel form.



- Other forms of hydroxyl-ion supply which can be used for this reaction are found in hydroxides of Li, Na, K, Rb, Cs, Ca, Mg, Ba, Sr or in form of organic bases or
20 quaternary hydroxides such as tetramethyl ammonium hydroxide etc.

- After separating the precipitated hydroxides from the remaining soluble fluoride, the latter is heated to its boiling point or a temperature approaching boiling point,
25 whereby, in the case of ammonia (as preferred base) it is driven off. On further concentration of the solution, the thereby present ammonium fluoride undergoes decomposition according to



water, and both water and leachant can be used over and over again.

If a hydroxide other than ammonium hydroxide is used the hydroxide cations may be removed by chemical means or 5 by ion exchange to regenerate the fluoride etchant solution.

The process may be presented in more detail by the flowsheet (Fig. 1) which illustrates one version of the fluoride recovery method in relation to the whole 10 demineralization process. Variations of this process, involving alternative types of reactors, filters, centrifuges, evaporators, stills, condensers, absorbers and other equipment, fall within the scope of the invention.

15 Feed coal 1, suitably sized and optionally precleaned by physical methods or otherwise to remove part of the mineral matter, is contacted in an extraction reactor 2 with an aqueous fluoride reagent 3 which acts as a leachant for minerals in the coal. The extraction reactor 20 may operate continuously or batchwise at ambient temperature or thereabouts, although any temperature between 0 and 100°C is feasible. A residence time of 1-12 hours at 20°C has been found appropriate in laboratory batch tests, but the optimum conditions vary. 25 with coal type, particle sizing and reactor design and are not limited to these ranges. The reaction mixture is then separated in a filter or centrifuge 4, appropriately coated with non-mineral containing, and thus fluoride resistant material, with washing to produce leached coal 5 30 as a solid product and a filtrate 6 plus washings. The leached coal 5 may be further purified in 7 by countercurrent washing with water, applied in conjunction with other reagents if required, or by other known methods, to produce a low-ash coal 8 which has been 35 substantially freed of mineral matter and or residual

leaching reagents, especially fluorides.

The filtrate and washings from 4 and 7 enter a precipitation reactor 9 to which ammonia or ammonium hydroxide 10 is also admitted in quantities sufficient to 5 deposit silicon, aluminium, and other elements in the form of hydroxides, hydrated oxides or their variants (eg. silicic acids or silica gel). After a sufficient time in this reactor, which may operate continuously or batchwise, the reaction mixture comprises a slurry of solid particles 10 in the presence of the co-product solution. This slurry passes to a filter or centrifuge 11 or equivalent device, preferably equipped with cake-washing facilities, where the mineral matter is separated from the filtrate containing soluble fluorides. The filtrate passes to a 15 heated decomposer 12 operating either batchwise or continuously at a temperature between ambient and the boiling point of the solution. Under these conditions the equilibrium in the ammonium fluoride/hydrofluoric acid system is substantially shifted, ammonia is liberated, and 20 the residual liquid phase can be regarded as a solution of ammonium fluoride, ammonium bifluoride and hydrofluoric acid. The vapour leaving 12 contains ammonia gas and steam which can be recovered in a condenser 13 as a solution of ammonium hydroxide 10, suitable for recycling 25 to 9.

After removing substantially all displacable ammonia in 12, the liquid may be subjected to evaporation or fractional distillation 14 to concentrate the fluoride solution to any desired concentration before recycling it 30 as 3 to 2. The overhead product is high-purity water vapour which, upon condensing in 15, yields high-purity water for washing purposes in 7 and 11. If there is an unacceptably high level of specific contaminants such as fluoride ions in this water, it may be passed through an 35 ion-exchange column 16 containing anionic exchange

materials before re-use.

Before concentration the recycled fluoride solution is monitored for undesirable impurities. In case of presence of iron or other cationic materials which may 5 have passed through the precipitation reaction, the solution can optionally be purified by precipitating these impurities with ammonium carbonate. This precipitate can be removed by filtration and the solution can then be concentrated, whereby excess ammonium carbonate will 10 undergo decomposition through loss of carbon dioxide and finally on concentration through loss of ammonia giving the desired ammonium bifluoride solution.

The invention as outlined provides a simple, low-temperature, atmospheric-pressure method for avoiding 15 contamination of air and water resources while effectively recovering and recycling fluorides, ammonia and high-purity water. Only small losses of these materials in the cleaned coal and mineral byproduct need result, thus requiring only low expenditures for make-up chemicals 20 and water. The mineral byproduct may have economic value or it may be disposed of in an innocuous landfill or minefill.

The results obtainable by application of the invention may be further understood from the following 25 example:

Example of fluoride recovery in coal refining.

64 g of moist (21% H₂O) Liddell coal (approx. 50 g dry basis) which had been previously up-graded in a float/sink separation step, using 1.5 gravity sulphuric acid at room 30 temperature, was mixed in a plastic beaker with 75 cc hydrofluoric acid (20%). The mixture was left at room temperature for two hours with occasional stirring, using a plastic rod. After removal of the acid by vacuum filtration, using plastic filtration equipment, the filter 35 cake was washed with 25 cc HF (20%) and then with 10 lots

of 50 cc pure water, giving a total filtrate of approximately 700 cc. The coal was allowed to dry at room temperature. Its ash content was reduced from an initial 5% to 0.5%. The total amount of hydrofluoric acid used in 5 this operation was 50cc of 40% w/w HF or 20 g HF (100% = 1 mole). The combined filtrates were neutralised with semi-concentrated (15%) aqueous ammonia liquor. After addition of 117 cc of ammonia, a pH value of 5 was reached (indicator paper), and a fine-crystalline precipitate 10 began to form. The crystals were allowed to settle overnight and were removed by filtration to give 3.5 g dry material analysed as triammonium hexafluoro-aluminate $(\text{NH}_4)_3\text{AlF}_6$, also known under its trivial name ammonium cryolite. Thereby, a selective recovery of 15 aluminium from solubilised ash constituents of coal is possible.

The further addition of ammonia liquor (20cc) brought about a rapid change in pH value, and silica precipitated out as a gel. The precipitate was washed several times 20 with water to remove adhering fluoride solution, and the combined filtrate was evaporated in a platinum dish until a solid crust formed on the surface of the solution. On cooling, a crystalline precipitate of ammonium fluoride formed, which was removed by filtration. The mother 25 liquors were concentrated further and the total crystalline product was heated for a short period to remove as much adhering water as possible. Obtained were 34.1 g crystals of ammonium fluoride of unknown composition. The fluoride content was analysed to be 30 47.3%, which constitutes a recovery of 16.1 g F in soluble form and 2 g F (in the ammonium cryolite) in insoluble form. The total recovery is therefore 18.1 g out of 19 g F or 95.2%.

In a blank experiment, hydrofluoric acid was 35 neutralised with ammonia and evaporated as described

before. The crystals obtained (16.5g) had 44.7% F content, giving a somewhat lower recovery. A total recovery of all fluoride in soluble form was probably not achieved in this case due to losses from the open system
5 which can be avoided, if a suitable closed system is available.

Other Examples

1. (a) A coking coal from the Bulli seam was floated with sulphuric acid as under Example 1(a) Part
10 1. The water-washed floats, while still wet with an ash content of 5.5% d.b. were suspended in a plastic beaker with 20% aqueous hydrogen fluoride and left 3 hours. The coal was washed by addition of water, filtered in a plastic Buchner funnel using hardened Whatman Filter paper. The coal was vacuum dried and its ash content found to be 0.36%.
- 15 (b) When the same coal was ball-milled and then treated as for Example 1(a) the fluoride treatment lowered the ash result to only 1.05%.
- 20 2. Coking coal from the Bulli seam (see Example 2 Part 1) having 5.9% ash value after initial upgrading was treated with 20% HF solution and worked up as specified under Example 1(a). The coal was demineralised to an ash value of 0.36%.
- 25 3. A soft coking coal from the Hunter Valley (Liddell) with an ash yield of 3.6% after upgrading was treated with aqueous HF (20%) at room temperature and worked up as previously described. The ash value obtained was 0.25%.
- 30 4. A coking coal from southern N.S.W. (Wongawilli) was upgraded by ball-milling and acid extraction to an ash value of 6.4%. When this coal was then digested with 20% aqueous HF at room temperature and the acid removed after 3 hours,

the coal had an ash content of 0.26%.

5. A steaming coal from N.S.W. (Ulan) with a particle size range of -250 + 75 microns had an ash value of 9.5% after sink-float treatment at SG = 1.5 in either perchloroethylene (admixed with heavier liquid) or sulphuric acid. The dried product free from organic liquid or the acid-free wet coal was left with 20% HF at room temperature overnight, and then filtered and washed. The ash content of the coal was lowered to 0.25% in each case.
- 10
6. The coal from Example (5) with a particle size range from -125 to +63 micron had an ash content of 8.5% after gravity separation. When treated as under Example (5), the ash content was found to be 0.25%.
- 15
- It will be recognised by persons skilled in the art that numerous variations and modifications may be made to the invention as described above without departing from 20 the spirit or scope of the invention as broadly described.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process for recycling fluoride following demineralizing bituminous coal or other mineral containing carbonaceous material by leaching the carbonaceous material with an aqueous fluoride etchant solution, the improvement comprising reacting the spent leachant with a ~~waste~~^{water} soluble hydroxide ion source to precipitate at least some of the minerals dissolved in the leachant, removing the precipitate therefrom and treating the resultant fluoride solution to regenerate an effective fluoride etchant solution.



~~THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:~~

1. In a process for demineralizing bituminous coal or other mineral containing carbonaceous material by leaching the carbonaceous material with an aqueous fluoride etchant solution, the improvement comprising reacting the spent leachant with a waste soluble hydroxide ion source to precipitate at least some of the minerals dissolved in the leachant, removing the precipitate therefrom and treating the resultant fluoride solution to regenerate an effective fluoride etchant solution.
2. The process according to claim 1 wherein the aqueous fluoride leachant is a solution of ammonium fluoride or bifluoride with or without hydrofluoric acid, and with or without other salts or organic materials.
3. The process according to claims 1 and 2, in which the precipitation reaction is conducted between ambient temperature and the boiling point of the solution with sufficient time to ensure that all or most of the dissolved minerals are deposited in a form that enables them to be readily removed by filtration or centrifugation.
4. The process according to claim 3 in which the precipitation reaction is conducted over a period of 0.2 to 5 hours.
5. The process according to claims 1 and 2 in which the recovered fluoride solution may be purified, if necessary, by precipitating out impurities with ammonium carbonate or by introduction of carbon dioxide into the basic fluoride solution and the separation of these impurities from the fluoride solution by filtration or centrifugation.
6. The process according to claims 1 and 2 in which the decomposition of the recovered fluoride solution to yield ammonia and water vapour is conducted at a temperature substantially above ambient.
7. A process according to claim 6 in which the temperature is between 50°C and the boiling point of the



solution under atmospheric pressure.

8. The process according to claim 6 whereby water and ammonia are substantially removed above ambient temperature by applying a vacuum.

9. The process according to claims 1 and 2 in which the regenerated fluoride leachant is concentrated under normal pressure or in vacuo to the extent necessary to make it suitable for recycling as a coal demineralizing reagent.

10. The process according to claims 1 and 2 in which the recovery and recycling of reagents and wash water is conducted in such a way as to approximate a closed system with respect to these materials.

11. A clean coal product with a typical ash yield between 0.1 and 1% on a dry basis, but not restricted to these limits, made by a process defined by any preceding claim.

12. A mineral-bearing byproduct or products derived therefrom, made by extracting ash-forming mineral matter from coal by a process defined by any preceding claim.

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